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### **JAPANESE / ENGLISH TRANSLATION OF**

**Source: Japanese Patent Application JP 2004 – 143353 A**

**Title of the Invention: Polyester Resin Composition for Calendering  
and Application Thereof**

**Your Ref: No. 5839**

**For: Eastman Chemical Company -  
Library and Information Services (LibrIS)**

(19) Japanese Patent Office (JP)

(11) Unexamined Patent Application No:

**(12) Unexamined Patent Gazette (A)**

**Kokai 2004-143353**

**(P2004-143353A)**

(43) Date of Publication: May 20, 2004

(51) Int. Cl.<sup>7</sup>

C 08 G 63/199

B 29 C 43/24

C 08 J 5/00

C 08 K 5/00

C 08 L 67/00

FI

C 08 G 63/199

B 29 C 43/24

C 08 J 5/00 CFD

C 08 K 5/00

C 08 L 67/00

Subject codes (reference)

4F071

4F204

4J002

4J029

Request for Examination: Not yet submitted

Number of Claims: 4 OL

(Total of 10 pages [in original])

(Continued on last page)

(21) Application No.: 2002-312022 (P2002-312022)

(22) Date of Filing: October 28, 2002

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**(54) [Title of the Invention]**

**Polyester Resin Composition for Calendering  
and Application Thereof**

**(57) [Summary]**

**[Object]** An object of the present invention is to provide a polyester resin composition that solves the problems of prior art, has excellent calendering characteristics, is readily recycled, is less likely to produce hydrogen chloride gas, dioxins, and other toxic gases when discarded or burned, and has excellent environmental compatibility, and to provide calendered articles composed of the resin composition.

**[Means of Achievement]** A polyester resin composition, characterized by comprising a copolyester resin whose dicarboxylic acid component is composed mainly of terephthalic acid and whose diol component is composed mainly of ethylene glycol and spiroglycol, wherein the latent heat of crystallization of the copolyester resin during cooling is 4 J/g or less, as measured with a differential scanning calorimeter (DSC), and the glass transition temperature is 90°C or higher.

**[Claims]**

**[Claim 1]**

A polyester resin composition for calendering, characterized by comprising a copolyester resin whose dicarboxylic acid component is composed mainly of terephthalic acid and whose diol component is composed mainly of ethylene glycol and spiroglycol, wherein the latent heat of crystallization of the copolyester resin during cooling is 4 J/g or less, as measured with a differential scanning calorimeter (DSC), and the glass transition temperature is 90°C or higher.

**[Claim 2]**

The polyester resin composition for calendering according to claim 1, characterized by comprising a lubricant.

**[Claim 3]**

The polyester resin composition for calendering according to claim 1 or 2, characterized in that the copolyester resin has a melt flow rate (hereinafter referred to as MFR) of 3.0 g/10 minutes or lower at a resin melt temperature of 200°C, and an MFR of 3.0 g/10 minutes or higher at a resin melt temperature of 250°C.

**[Claim 4]**

Molded articles obtained by calendar-molding the polyester resin composition according to any of claims 1 to 3.

**[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]**

The present invention relates to a polyester resin composition for calendering and to calender-molded articles thereof, and more specifically relates to a polyester resin composition

for calender-molding and to molded articles composed of a polyester resin composition that has excellent calendering characteristics, is readily recycled, is less likely to produce hydrogen chloride gas, dioxins, and other toxic gases when discarded or burned, and has excellent environmental compatibility.

**[0002]**

**[Prior Art]**

Calendering is an economical and efficient method for manufacturing films and sheets from thermoplastic resin. Films and sheets obtained by calendering ordinarily have a uniform thickness of 0.05 mm to 2 mm, are readily thermoformed into a variety of shapes, and are used in a wide variety of fields including the civil engineering and construction fields, as well as in products such as furniture, machine parts, and automatic components. Polyvinyl chloride resin is conventionally used as a resin for calendering because it is readily molded. However, environmental problems have been pointed out with regard to polyvinyl chloride resins, which produce hydrogen chloride gas, dioxins, and other toxic gases when discarded or burned. For this reason, polyester resin is actively being studied as a modern alternative material. Nevertheless, polyester resin commonly has a low melt viscosity, and there is a drawback in that drawdown occurs during calender molding, and the moldability is poor. Furthermore, since release from the calender roll is poor and molding films and sheets with a smooth surface is difficult, there is currently no satisfactory alternative resin (refer to patent references 1, 2, and 3).

**[0003]**

**[Patent Reference 1]**

Japanese Patent 3280374 (Page 3)

**[Patent Reference 2]**

Japanese Patent 3300674 (Page 2)

**[Patent Reference 3]**

Japanese Patent 3305273 (Page 2)

[0004]

**[Problems to Be Solved by the Invention]**

An object of the present invention is to provide a polyester resin composition that solves the problems of the above-described prior art, has excellent calendering characteristics, is readily recycled, is less likely to produce hydrogen chloride gas, dioxins, and other toxic gases when discarded or burned, and has excellent environmental compatibility, and to provide calendered articles composed of the resin composition.

[0005]

**[Means Used to Solve the Above-Mentioned Problems]**

The above-described objects can be achieved by a polyester resin composition characterized in comprising a copolyester resin whose dicarboxylic acid component is composed mainly of terephthalic acid and whose diol component is composed mainly of ethylene glycol and spiroglycol, wherein the latent heat of crystallization of the copolyester resin during cooling is 4 J/g or less, as measured with a differential scanning calorimeter (DSC), and the glass transition temperature is 90°C or higher.

[0006]

**[Embodiments of the Invention]**

The acid component of the copolyester resin according to the present invention is mainly composed of terephthalic acid, but a small amount of another dicarboxylic acid component may also be used. Specific examples include adipic acid, oxalic acid, malonic acid, succinic acid, azelaic acid, sebacic acid, and other aliphatic dicarboxylic acids; isophthalic acid, 2,6-naphthalenedicarboxylic acid, diphenyl dicarboxylic acid, and other aromatic dicarboxylic acids; cyclohexane dicarboxylic acid and other alicyclic dicarboxylic acids; and dimer acids. These may be used alone or in a combination of two or more, but the amount is preferably 10 mol% or less of the entire dicarboxylic acid component.

[0007]

The glycol component of the copolyester resin of the present invention is mainly composed of ethylene glycol and spiroglycol, but a small amount of another glycol component may also be used. Specific examples include diethylene glycol, butanediol, neopentyl glycol, propylene glycol, hexamethylene glycol, 1,4-cyclohexane dimethanol, polyalkylene glycol, and

bisphenol A or bisphenol S diethoxy compounds. These may be used alone or in a combination of two or more, but the amount is preferably 10 mol% or less of the entire diol component.

[0008]

The copolyester resin of the present invention is manufactured by subjecting a material whose main components are terephthalic acid or an ester-forming derivative thereof, and ethylene glycol and spiroglycol to an esterification reaction, a liquid-phase polycondensation reaction, an optional solid-phase polymerization reaction, and a heat treatment with at least one type of compound that contains a metallic element selected from the group composed of antimony, titanium, germanium, tin, and zinc as a catalyst.

[0009]

The esterification reaction is carried out at a temperature of 240 to 280°C and a pressure of 20 to 300 kPa. In this case, only the water generated by the esterification reaction between terephthalic acid and the diol component is discharged out of the system. In the esterification reaction, a polyester with few byproducts is obtained when a basic compound is added in a small amount. Examples of such a basic compound include triethylamine, tributylamine, benzyl methylamine, and other tertiary amines; and tetraethylammonium hydroxide, tetrabutylammonium hydroxide, trimethylbenzylammonium hydroxide, and other quaternary amines.

[0010]

The liquid-phase polycondensation reaction is carried out in the presence of at least one type of compound catalyst that contains a metallic element selected from the group composed of antimony, titanium, germanium, tin, and zinc at a temperature of 250 to 300°C and under a reduced pressure of 13.3 to 665 Pa. In the liquid-phase polycondensation reaction, the unreacted diol component is distilled out of the system from the lower-order condensate between the terephthalic acid and diol component obtained in the esterification reaction.

[0011]

Examples of the polymerization reaction catalyst used in the present invention include germanium dioxide, germanium tetraethoxide, germanium tetrabutoxide, and other germanium compounds; antimony trioxide, antimony pentoxide, antimony tartrate, antimony acetate, and other antimony compounds; tetrabutyl titanate, and other titanium compounds; tin acetate, and other tin compounds; and zinc acetate, and other zinc compounds. Among these, germanium

compounds are preferred from the aspect of the color tone and transparency of the resulting resin. The polymerization reaction catalyst is added as an aqueous solution or ethylene glycol solution having a prescribed catalyst concentration.

[0012]

From the aspect of polymerization reaction velocity, the added amount of the polymerization reaction catalyst is preferably  $1 \times 10^{-5}$  to  $1 \times 10^{-3}$  mol per mole of the acid component of the resulting copolyester resin.

[0013]

A stabilizer may be added in the liquid-phase polymerization reaction step in order to prevent thermal decomposition of the copolyester resin, and other side reactions. Examples of the stabilizer include trimethyl phosphoric acid, triethyl phosphoric acid, and other phosphoric acid esters; phosphorous acid, polyphosphoric acid, and other phosphorus compounds; and compounds composed of hindered phenols.

[0014]

From the aspect of polymerization reaction velocity, the added amount of the stabilizer is preferably  $1 \times 10^{-5}$  to  $1 \times 10^{-3}$  mol per mole of the acid component of the resulting copolyester resin.

[0015]

The intrinsic viscosity of the copolyester of the present invention is preferably 0.60 to 0.90 dL/g, and is more preferably 0.70 to 0.90 dL/g. If the intrinsic viscosity is less than 0.60 dL/g, the resin melt viscosity required for extrusion molding cannot be obtained. If the intrinsic viscosity exceeds 0.90 dL/g, melting the resin becomes difficult and foreign matter caused by unmelted resin more readily occurs in the molded article.

[0016]

In the copolyester resin of the present invention, the latent heat of crystallization during cooling is 4 J/g or less, as measured using a DSC (differential scanning calorimeter) when the temperature is raised from room temperature to 300°C at a temperature increase rate of 10°C/minute, and is then immediately reduced to room temperature at a temperature decrease rate of 10°C/minute. If the latent heat of crystallization during cooling exceeds 4 J/g, the crystallinity of the copolyester increases, and since processing at high temperatures is required during calendering, the hydrolysis reaction of the polyester is promoted, and the calendering

characteristics are markedly worsened. The latent heat of crystallization during cooling can be kept at 4 J/g or less by adjusting the spiroglycol content, for example. The spiroglycol content is preferably 10 mol% or higher with respect to the entire diol component, and the content is more preferably 20 to 80 mol%.

[0017]

The copolyester of the present invention is provided with a glass transition temperature of 90°C or higher, as measured using a DSC (differential scanning calorimeter), by increasing the temperature from room temperature to 300°C at a temperature increase rate of 10°C/minute. When the glass transition temperature is less than 90°C, the tendency of the copolyester resin to adhere to the calendering roll increases during calendering, and the release of the sheet from the roll is markedly reduced. To achieve a glass transition temperature of 90°C or higher, a method can be used in which the spiroglycol content is kept at 17 mol% or higher with respect to the entire diol component, for example.

[0018]

The copolyester of the present invention preferably has a melt flow rate (hereinafter referred to as MFR) of 3.0 g/10 minutes or lower at a resin melting temperature of 200°C, and an MFR of 3.0 g/10 minutes or higher at a resin melting temperature of 250°C. If the MFR at a resin melting temperature of 200°C is excessively high, drawdown tends to occur during calendering. If the MFR at a resin melting temperature of 250°C is excessively low, an excessive load may be placed on the rotation of the calender roll during calendering.

[0019]

The MFR is measured in the present invention in accordance with JIS K7210. More specifically, copolyester resin is loaded into a cylinder with an inside diameter of 9.55 mm and a length of 162 mm, a plunger with a weight of 2,160 g and a diameter of 9.48 mm is placed on the resin melted at the test temperature, a load is uniformly applied to the polymer melt, and the flow velocity of the polymer melt extruded from an orifice with a diameter of 2.095 mm disposed in the center of the cylinder is taken to be the melt flow rate.

[0020]

A polyfunctional compound having three or four ester bond-forming functional groups in the molecule is preferably added to the copolyester resin of the present invention in the manufacturing step thereof in order to improve the calendering characteristics. A polyfunctional



compound is a compound that forms an ester bond via reaction with the carboxyl group or hydroxyl group in the polyester molecular chain, and is more specifically a compound having a carboxyl group, a hydroxyl group, or a methyl ester group, ethyl ester group, or other alkyl ester group. A cross-linking structure is formed in the polyester molecular chain by adding such a polyfunctional compound, thereby improving the melt properties and enhancing calendering characteristics.

**[0021]**

Specific examples of a polyfunctional compound include pentaerythritol, trimethylolpropane, trimellitic acid and anhydrides thereof, pyromellitic acid and acid anhydrides thereof, and trimesic acid and other polyfunctional alcohols and acids. The polyfunctional compound content is preferably 0.05 to 2.0 mol% with respect to the entire amount of polymer, and is more preferably 0.2 to 0.5 mol%. A polyfunctional compound content in this range is preferred because the melt properties are improved by moderate cross linking, the calendering characteristics are enhanced, and the occurrence of unmelted substances in the molded articles can be inhibited.

**[0022]**

The polyester resin composition of the present invention preferably contains an additive for preventing the copolyester from adhering to the calender roll. The amount of additive contained in the polyester resin composition is commonly 0.01 to 10 parts by weight per 100 parts by weight of the copolyester resin. The optimum amount of additive to be used can be determined using factors known in the technological field, but the amount varies in accordance with the calendering apparatus, the polyester resin composition, the calendering conditions, and the thickness of the sheet or film obtained by calendering. When the amount of addition is considerable, the resulting sheet or film will have poor surface smoothness.

**[0023]**

A suitable additive for use in the present invention is one that is known in the technological field of calendering, and that contains an internal lubricant, a slip agent, or a combination thereof. Examples of such an additive include fatty acid amides such as erucic amide and stearamide; metal salts of organic acids such as calcium stearate and zinc stearate; fatty acids such as stearic acid, oleic acid, and palmitic acid; hydrocarbon waxes such as ester,

paraffin wax, polyethylene wax, and polypropylene wax; chemically modified polyolefin wax; glycerol stearate; talc; and acrylic copolymers.

[0024]

A common antioxidant may be added to the polyester resin composition of the present invention in order to prevent oxidative decomposition of the molten or semi-solid material on the calender roll. Examples of a suitable antioxidant include hindered phenol compounds such as Irganox 1010 (manufactured by Ciba Specialty Chemicals) and Ethanox 330 (manufactured by Ethyl Corporation), and phosphorus compounds such as Irgafos (manufactured by Ciba Specialty Chemicals) and Weston (manufactured by GE). These antioxidants may be used alone, or in a combination of two or more. The amount of antioxidant contained in the polyester resin composition is commonly 0.01 to 10 parts by weight per 100 parts by weight of the copolyester resin.

[0025]

The method for manufacturing a calender-molded article according to the present invention is not particularly limited, and a known calendering apparatus may be used. In common practice, the calendering apparatus has no less than two, but preferably four or more adjacent metal rolls. The copolyester resin composition of the present invention is fed in the form of pellets, a powder, or a melt between two metal rolls. The metal rolls are arranged in a line, or in the form of an "L," an inverted "L," or a "Z." In common practice, the composition is calendered with the surface temperature of the metal rolls at a temperature of 80 to 160°C higher than the glass transition temperature of the copolyester.

[0026]

In order to prevent polymer degradation due to hydrolysis during molding, the copolyester resin composition is preferably pre-dried or excess moisture is expelled during calendering. With this method, films and sheets with excellent surface smoothness can be very economically produced with a uniform thickness from the copolyester resin composition. The polyester calendering method disclosed in Japanese Patent 3280374 is a typical example of a method in which such a calendering apparatus is used.

[0027]

**[Effect of the Invention]**

The copolyester resin composition of the present invention can be used to manufacture calender-molded articles composed of a polyester resin composition that has excellent calendering characteristics, is readily recycled, is less likely to produce hydrogen chloride gas, dioxins, and other toxic gases when discarded or burned, and has excellent environmental compatibility.

[0028]

**[Working Examples]**

The present invention is described below in detail using working examples.

The measuring methods and evaluation of the properties were carried out in accordance with the methods described below.

[0029]

(1) Intrinsic Viscosity (IV)

Copolyester resin was dissolved in a mixed solution composed of phenol/tetrachloroethane in a ratio of 60/40 (parts by weight), and the intrinsic viscosity was measured at 20°C using an automatic viscometer SS-270LC manufactured by Shibayama Scientific Co.

[0030]

(2) Copolymerization Ratio

Copolyester resin was dissolved in a mixed solution composed of trifluoroacetic acid-d and heavy chloroform (1:1) and then mixed with tetramethylsilane to form a sample, and the copolymerization ratio was measured using an FT-NMR (300MG, manufactured by Varian).

[0031]

(3) Glass Transition Temperature (T<sub>g</sub>), Latent Heat of Crystallization ( $\Delta H_c$ )

About 10 mg of copolyester resin was metered out and T<sub>g</sub> was measured using a differential scanning calorimeter (DSC-7, manufactured by PerkinElmer) at a temperature increase rate of 10°C/minute between room temperature and 300°C, and  $\Delta H_c$  was measured at a temperature decrease rate of 10°C/min between 300°C and room temperature.

[0032]

(4) Melt Flow Rate (MFR)

The melt flow rate was measured in accordance with JIS K7210 by using a melt indexer TYPE C-5059 manufactured by Toyo Seiki Seisaku-sho. More specifically, copolyester resin was loaded into a cylinder with an inside diameter of 9.55 mm and a length of 162 mm, a plunger with a weight of 2,160 g and a diameter of 9.48 mm was placed on the resin melted at test temperatures of 200°C and 250°C, a load was uniformly applied to the polymer melt, and the flow velocity of the polymer melt extruded from an orifice with a diameter of 2.095 mm disposed in the center of the cylinder was measured.

[0033]

(5) Calendering Characteristics

Sheets with a thickness of 0.5 mm were molded from copolyester resin using a calendering apparatus having four metal rolls with the temperature of the metal roll surfaces set to 180°C. The release from the metal roll and the smoothness of sheet surfaces were then evaluated.

(Release Properties)

○: Very readily released from the metal roll

×: Released from the metal roll with difficulty

(Surface Smoothness)

○: The surface of the sheet was smooth and flat

×: The surface of the sheet was rough and unsmooth

[0034]

(6) Sheet Properties

The transparency and heat resistance of the resulting sheets were measured.

(Transparency)

Transparency was measured in accordance with JIS K7105 using a haze meter (Haze Meter 300A manufactured by Nippon Denshoku Industries).

(Heat Resistance)

The glass transition temperature was measured using a differential scanning calorimeter (DSC-7, manufactured by PerkinElmer) at a temperature increase rate of 10°C/minute.

[0035]

(Manufacture of Copolyester Resin)

Ethylene glycol was loaded into a stainless steel autoclave and subjected to an esterification reaction with a prescribed amount of terephthalic acid at 250°C and 200 kPa until the molar ratio of the glycol component reached 1.2 with respect to the acid component. After the esterification reaction was completed, a prescribed amount of spiroglycol, antimony trioxide catalyst, and trimethyl phosphate was added, and a polycondensation reaction was carried out at 280°C under a reduced pressure of 66 Pa. The copolymer composition, IV, Tg, and MFR of the resulting copolyester resin were evaluated; the results are shown in Tables 1 and 2.

[0036]

(Calendering)

**Working Examples 1 to 6, Comparative Examples 1 to 6**

The resulting polyester resin and lubricant were fed to a calendering apparatus with four metal rolls in the ratios shown in Tables 3 to 5, and sheets with a thickness of 0.5 mm were molded at a metal roll temperature of 180°C (P-1 at 280°C, and P-2 at 250°C). The calendering characteristics and the physical properties of the resulting sheet were measured. The results are shown in Tables 3 to 6. Sheets with excellent surface smoothness could not be obtained in comparative examples 1 to 4, and the physical properties of the sheets could not be evaluated.

[0037]

[Table 1]

	Intrinsic Viscosity (dL/g)	SPG Ratio (mol%)	Tg (°C)	ΔHc (J/g)
P-1	0.72	5	80	30
P-2	0.71	10	85	0
P-3	0.71	17	90	0
P-4	0.68	30	101	0
P-5	0.69	45	106	0
P-6	0.65	70	120	0
P-7	0.80	CHDM30	80	0
P-8	0.75	IPA30	74	0

SPG: Spiroglycol

CHDM: Cyclohexane dimethanol

IPA: Isophthalic acid

[0038]

[Table 2]

	MFR (g/10 minutes)	
	200°C	250°C
P-1	Not dissolved	Not dissolved
P-2	Not dissolved	3.20
P-3	0.43	5.30
P-4	0.83	10.15
P-5	0.62	10.72
P-6	0.41	5.47
P-7	3.80	13.50
P-8	9.00	32.27

[0039]

[Table 3]

		Working Example 1	Working Example 2	Working Example 3
Copolyester resin		P-3	P-4	P-5
Lubricant (Zinc stearate)		–	–	–
Calendering characteristics	Release properties	○	○	○
	Surface smoothness	○	○	○
Sheet properties	Transparency	1.2%	1.0%	1.0%
	Heat resistance	90°C	100°C	105°C

[0040]

[Table 4]

		Working Example 4	Working Example 5	Working Example 6
Copolyester resin		P-6	P-3	P-3
Lubricant (Zinc stearate)		–	0.1%	0.2%
Calendering characteristics	Release properties	○	○	○
	Surface smoothness	○	○	○
Sheet properties	Transparency	1.0%	3.0%	4.7%
	Heat resistance	120°C	90°C	90°C

[0041]

[Table 5]

		Comparative Example 1	Comparative Example 2	Comparative Example 3
Copolyester resin		P-1	P-2	P-7
Lubricant (Zinc stearate)		—	—	—
Calendering characteristics	Release properties	×	×	×
	Surface smoothness	×	×	×
Sheet properties	Transparency	—	—	—
	Heat resistance	—	—	—

[0042]

[Table 6]

		Comparative Example 4	Comparative Example 5	Comparative Example 6
Copolyester resin		P-8	P-7	P-7
Lubricant (Zinc stearate)		—	0.5%	—
Lubricant (Montanic acid ester)		—	—	0.5%
Calendering characteristics	Release properties	×	○	○
	Surface smoothness	×	○	○
Sheet properties	Transparency	—	14.5%	20.0%
	Heat resistance	—	80°C	80°C

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(51) Int. Cl.<sup>7</sup>  
B29K 67:00  
B29L 7:00

FI  
B29K 67:00  
B29L 7:00

Subject codes (reference)

F Terms (Reference)

4F071 AA15 AA20 AA33 AA45X AA71 AA76 AA86 AA87 AA88 AA89  
AB26 AC09 AC10 AC12 AE11 AH03 AH04 BA01 BB04 BC01  
4F204 AA24C AA24E AB07 AG01 FA06 FB02 FE30 FF01  
4J002 AE042 BB032 BB122 BB202 BG042 CF051 EF036 EG036 EG046 EH036  
EH046 EP016 FD172 FD176 GG02  
4J029 AA03 AC02 AD01 AD07 AD08 AE03 BA03 BD10 CB06A HA01  
HB01 JA091 JB131 JB171 JF181 JF321 JF361 JF371 JF471 KE03  
KE09 KE12